

## 1,1'-Bis(thiocyanatomercurio)ferrocene as Ligand towards $M(NCS)_2$ [ $M=Mn(II)$ , $Co(II)$ , $Ni(II)$ , $Cu(II)$ , $Zn(II)$ ]

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Complexes having three different metal atoms have been prepared by reacting 1,1'-bis(thiocyanatomercurio)-ferrocene with  $M(NCS)_2$  [ $M=Mn(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$ ,  $Zn(II)$ ]. The complexes have been referred to as Lewis acid and have molecular formula  $Fe(C_5H_4HgSCN)_2M(NCS)_2$ . They have unsaturation at M, hence have been reacted with nicotinamide and 2,2'-bipyridyl and adducts of molecular formula  $Fe(C_5H_4HgSCN)_2M(NCS)_2L_x$  [ $x=2$  when nicotinamide and 1 when bipyridyl] have been isolated. The Lewis acids and the adducts have been characterized by elemental analysis, molar conductance, magnetic moment, infrared and electronic spectral studies. These studies reveal that the coordination geometry of M is tetrahedral in the Lewis acids of cobalt, zinc, and manganese. The geometry around M in the Lewis acids of nickel and copper is octahedral through axial bonding. The adducts have a bridged structure and the geometry around M is octahedral. Quantitative softness parameters have also been applied to derive certain information.

Complexes having two different metals have recently been reported.<sup>1-3</sup> Attempts have also been made<sup>4,5</sup> to prepare trimetallic complexes but no systematic studies could be made. In this paper, a new class of complexes having three different metals have been prepared and studied for the first time.

### Experimental

Reagent grade solvents were purified before use.  $M(NCS)_2 \cdot 2nia$  [ $M=Mn(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$ ,  $Zn(II)$  nia=nicotinamide] were prepared by direct reaction of nicotinamide and  $M(NCS)_2$  in ethanol. 2,2'-Bipyridyl (bpy) was used from fresh bottle. 1,1'-Bis(thiocyanatomercurio)-ferrocene (FBMT) was prepared as given below.

#### Preparation of 1,1'-Bis(thiocyanatomercurio)ferrocene.

9.2 g (0.25 mole) ferrocene was dissolved in 50 ml of benzene in a two necked flask. A homogeneous suspension of 16 g (0.25 mole) of mercury(II) acetate in 200 ml of methanol was separately prepared. This suspension was very slowly added to the solution of ferrocene through a dropping funnel, with continuous stirring. A dark brown clear solution was obtained. To this, a solution of 4.8 g (0.25 mole) KSCN in 10 ml of water was added, and stirred for 30 min. A yellow precipitate was formed which was filtered on büchner funnel and washed with petroleum ether. This yellow compound was a mixture of (thiocyanatomercurio) ferrocene and 1,1'-bis(thiocyanatomercurio)ferrocene.

**Separation of Mono and Bis Derivatives.** The yellow mass was placed in upper disc of the Soxhlet apparatus and the flask was filled with 25 ml of 1,2-dichloroethane and extracted for 30 min. A portion of yellow mass dissolved in 1,2-dichloroethane and its color became yellow. The yellow solution was collected and fresh 25 ml of pure 1,2-dichloroethane was added and again extracted for 30 min. The process was continued till there was no change in the color of 1,2-dichloroethane. On evaporation of the yellow extract impure (thiocyanatomercurio)ferrocene was obtained. The undissolved yellow residue was FBMT. This compound was purified by dissolving in dimethylsulfoxide (DMSO) and isolating the pure compound by addition of water. The analytical data of the bis derivative are; mp 145°C (decomp), sulfur calcd. 9.14%, found 8.85%, nitrogen calcd. 4% found 3.72%, mercury calcd. 57.14% found 56.01%.

#### Preparation of Lewis Acids: " $Fe(C_5H_4HgSCN)_2M(NCS)_2$ "

[ $M=Mn(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$ , and  $Zn(II)$ ]. FBMT was dissolved in a small quantity of DMSO and diluted to 200 ml by acetone.  $M(NCS)_2$  were similarly dissolved either in acetone or DMSO-acetone mixture separately.  $Mn(NCS)_2$  was however, dissolved in ethyl acetate. The solutions of FBMT and  $M(NCS)_2$  were mixed in 1:1 molar ratio and stirred for 24 h. Precipitate appeared in each case. When the quantity of DMSO became more the precipitates were obtained by addition of ethanol. The precipitates were filtered, washed with ethanol, and dried in vacuum. The compounds were recrystallized from acetone-ethanol mixture.

**Preparation of Adducts:  $Fe(C_5H_4HgSCN)_2M(NCS)_2L_x$  [ $x=2$  when L is nia and 1 when bpy].** The adducts were prepared by two methods. (1) A suspension or solution of the Lewis acids was prepared in acetone-ethanol mixture and mixed with an ethanol solution of nicotinamide in 1:2 molar ratio or with 2,2'-bipyridyl in 1:1 molar ratio and stirred for 24 h. In each case precipitate was formed, filtered, washed with ethanol, and dried in vacuum. The compounds were recrystallized from acetone-ethanol mixture. (2)  $M(NCS)_2 \cdot 2nia$  was dissolved in acetone. The corresponding manganese compound was dissolved in ethyl acetate. FBMT was dissolved in DMSO-acetone mixture. The solutions of  $M(NCS)_2 \cdot 2nia$  and FBMT were mixed in 1:1 molar ratio and stirred for 48 h. Precipitate was formed in each case which was filtered, washed with ethanol, and dried in vacuum. Recrystallized from acetone-ethanol mixture. The copper analog could not be prepared by this method.

**Analysis of the Complexes.** The complexes were analyzed for cobalt as anthranilate, and for nickel as dimethylglyoximate. Sulfur as sulfate and mercury as sulfide. Nitrogen was estimated by semimicro Kjeldahl's method. Analytical results along with melting points are presented in Table 1.

**Physical Measurements.** The molar conductance of the complexes were measured in DMSO using a Philip conductivity bridge model PR-9500. The molecular weights were determined in DMSO solution by cryoscopic method. The magnetic susceptibility measurements were made at room temperature by Gouy's method using  $CoHg(SCN)_4$  as standard. The diamagnetic corrections were made using Pascal's constants. Infrared spectra of the complexes were recorded as nujol mulls or as KBr pellets on a Pye Unicam sp 3-300 spectrophotometer in the range 4000–200  $cm^{-1}$ . Elec-

Table 1. Analytical Data of the Complexes

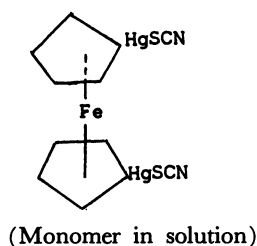
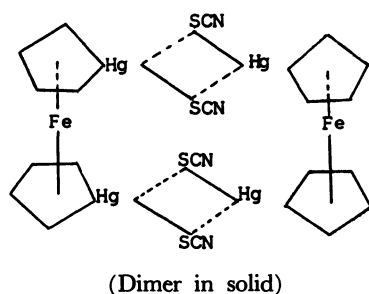
Complex	Color	Mp $\theta_m/^\circ\text{C}$	Sulfur %		Mercury %		Metal %		Nitrogen %		Molecular wt.		Molar Conductance $\text{cm}^{-1}\text{mhos/mol}$ M/1024
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Ni}(\text{NCS})_2$	Light green	240(d)	14.65	14.12	45.71	45.43	6.62	6.71	6.40	6.16	875	—	70.34
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Co}(\text{NCS})_2$	Blue	230(d)	14.65	14.16	45.71	45.27	6.62	6.80	6.40	6.21	875	—	58.62
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Cu}(\text{NCS})_2$	Light green	185(d)	14.54	14.26	45.45	45.12	7.15	7.82	6.36	6.19	880	—	30.58
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Zn}(\text{NCS})_2$	Light brown	178(d)	14.51	14.32	45.35	45.03	7.36	7.40	6.34	6.23	882	—	48.38
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Mn}(\text{NCS})_2$	Grey	164(d)	14.71	14.30	45.97	45.07	6.20	6.73	6.43	6.21	870	—	48.02
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Ni}(\text{NCS})_2(\text{bpy})$	Mustard	210(d)	12.42	12.33	38.83	38.21	5.63	5.82	5.43	5.31	1030	842	73.45
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Ni}(\text{NCS})_2(\text{nia})_2$	Brown	200(d)	11.44	12.20	35.77	35.13	5.18	5.29	5.00	4.94	1118	975	62.75
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Co}(\text{NCS})_2(\text{bpy})$	Dirty pink	190(d)	12.42	12.13	38.83	38.36	5.63	5.50	5.43	5.22	1030	872	70.29
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Co}(\text{NCS})_2(\text{nia})_2$	Dirty pink	195(d)	11.44	11.22	35.77	35.46	5.18	5.12	5.00	4.85	1118	913	60.23
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Cu}(\text{NCS})_2(\text{bpy})$	Mustard	175(d)	12.36	11.13	38.68	38.12	6.28	6.18	5.41	5.32	1035	924	50.44
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Cu}(\text{NCS})_2(\text{nia})_2$	Green	190(d)	11.39	11.01	35.60	35.32	5.60	5.70	4.98	4.79	1123	914	50.25
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Zn}(\text{NCS})_2(\text{bpy})$	Dirty white	162(d)	12.34	12.03	38.57	38.42	6.26	6.41	5.40	5.23	1037	842	43.28
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Zn}(\text{NCS})_2(\text{nia})_2$	Dirty white	185(d)	11.37	11.12	35.55	35.12	5.77	5.82	4.97	4.82	1125	932	43.08
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Mn}(\text{NCS})_2(\text{bpy})$	Light brown	180(d)	12.45	12.04	38.91	38.82	5.25	5.33	5.44	5.12	1028	—	43.13
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Mn}(\text{NCS})_2(\text{nia})_2$	Grey	170(d)	11.46	11.20	35.84	35.01	4.83	4.18	5.01	4.82	1116	—	43.00

(d)=decomp.

tronic spectra in the range 200—990 nm were recorded on Pye Unicam sp 5-500. The thermodynamics stability constant ( $\log K$ ), has been determined by spectrophotometric method.

### Results and Discussion

The spectra of FBMT were recorded in solid and solution phase. The solid phase spectra show the presence of three bands at 2190, 2120, and 2100  $\text{cm}^{-1}$  in  $\nu(\text{CN})$  region, two bands at 730 and 720  $\text{cm}^{-1}$  in  $\nu(\text{CS})$  region and two bands at 460 and 410  $\text{cm}^{-1}$  in  $\delta(\text{NCS})$  region. The band at 2190  $\text{cm}^{-1}$  disappears in solution. This shows that FBMT exists as dimer in solid phase like  $\text{CH}_3\text{HgSCN}^6$  as shown below.



In solution phase the thiocyanato bridge is broken and this becomes a monomer. The solution spectra have therefore, been taken for the purpose of comparison. The band at about 2120  $\text{cm}^{-1}$  in  $\nu(\text{CN})$  region, at about 740  $\text{cm}^{-1}$  in  $\nu(\text{CS})$  region and at about 450  $\text{cm}^{-1}$  in  $\delta(\text{NCS})$  indicate the presence of S-bonded thiocyanate

in FBMT.

Lewis acids:  $\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{M}(\text{NCS})_2$  [ $\text{M} = \text{Mn}(\text{II})$ ,

$\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Cu}(\text{II})$ ,  $\text{Zn}(\text{II})$ ].

The FBMT has been used as ligand and reacted with  $\text{M}(\text{NCS})_2$ . This results in the formation of a complex of general formula  $\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{M}(\text{NCS})_2$ . These compounds have been referred to as Lewis acids. Comparison of the infrared spectra of the FBMT with the Lewis acids shows that the position of  $\nu(\text{CN})$ ,  $\nu(\text{CS})$ , and  $\delta(\text{NCS})$  bands are changed. The  $\nu(\text{CN})$  band moves to about 2190  $\text{cm}^{-1}$ ,  $\nu(\text{CS})$  band to about 790  $\text{cm}^{-1}$  and  $\delta(\text{NCS})$  band to about 480  $\text{cm}^{-1}$ . The positions of these bands are indicative of the presence of thiocyanato bridge.<sup>7</sup> A band is also observed in 2070  $\text{cm}^{-1}$  to 2010  $\text{cm}^{-1}$  region. Band in this region is assigned to N-bonded terminal thiocyanate arising from  $\nu(\text{M}-\text{NCS})$ .<sup>8</sup>

The electronic spectra of the Lewis acid where M is  $\text{Co}(\text{II})$ , show the presence of two intense bands in the region 17450  $\text{cm}^{-1}$  and 10640  $\text{cm}^{-1}$  which are assigned to  $^4\text{A}_2 \rightarrow ^4\text{T}_2(\text{F})$  ( $\nu_3$ ) and  $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{P})$  ( $\nu_2$ ) transitions, respectively (Table 2). The  $D_q$  value derived from  $\nu_3$  and  $\nu_2$  bands is 541  $\text{cm}^{-1}$ . The positions of these bands and the magnetic moment values show that the cobalt is in tetrahedral geometry. The compound is nonconducting in nature. On the basis of these results the following structure (Fig. 1) can be proposed for this Lewis acid.

The infrared spectra of the Lewis acids where M is  $\text{Zn}(\text{II})$  or  $\text{Mn}(\text{II})$  are similar to the Lewis acid where M is cobalt(II). It can, therefore, be presumed that the structure of these Lewis acids is also similar to that in Fig. 1. The electronic spectra of Lewis acid where M is  $\text{Ni}(\text{II})$  show the presence of three bands in the region 27790, 16650, and 10400  $\text{cm}^{-1}$  which are assigned to  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})$  ( $\nu_3$ ),  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$  ( $\nu_2$ ), and  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}(\text{F})$  ( $\nu_1$ ), respectively. The  $D_q$  value derived from  $\nu_2$  and  $\nu_3$  bands is 1020  $\text{cm}^{-1}$  (Table 2). The spectra and magnetic moment values indicate the

Table 2. Infrared Spectral and Electronic Spectral Bands with Spectral Parameters

Complex	$\nu(\text{CN})$ $\text{cm}^{-1}$	$\nu(\text{CS})$ $\text{cm}^{-1}$	$\delta(\text{NCS})$ $\text{cm}^{-1}$	$\nu(\text{M-NCS})$ $\text{cm}^{-1}$	$\nu_3$ $\text{cm}^{-1}$	$\nu_2$ $\text{cm}^{-1}$	$\nu_1$ $\text{cm}^{-1}$	Dq $\text{cm}^{-1}$	B' $\text{cm}^{-1}$	$\beta$	$\mu_{\text{eff}}$ (BM)
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2$ (solid)	2190(w), 2120(s), 2100(s)	730(s), 720(m)	460(s), 410(sh)	—	—	—	—	—	—	—	—
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2$ (solution)	2120(s), 2070(m)	740(s), 720(w)	450(s), 420(m)	—	—	—	—	—	—	—	—
<b>Lewis acid</b>											
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Ni}(\text{NCS})_2$	2170(w), 2100(s)	780(s), 760(s)	470(s), 450(sh)	260(s), 240(sh)	27790	16650	10400	1020	906	0.87	3.07
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Co}(\text{NCS})_2$	2190(s), 2120(s)	790(s), 760(w)	480(sh), 460(s)	320(s), 295(s)	17540	10640	—	541	796	0.77	4.24
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Cu}(\text{NCS})_2$	2180(s), 2100(m)	760(s), 740(w)	480(w), 440(s)	265(s), 245(m)	—	—	—	—	—	—	1.92
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Zn}(\text{NCS})_2$	2160(sh), 2100(s)	770(m), 740(s)	470(s), 450(s)	325(s), 280(m)	—	—	—	—	—	—	—
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Mn}(\text{NCS})_2$	2180(s), 2110(w)	750(w), 720(s)	460(m), 450(s)	315(m), 285(s)	—	—	—	—	—	—	6.40
<b>Adduct</b>											
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Ni}(\text{NCS})_2(\text{bpy})$	2170(s), 2090(sh)	770(s), 740(s)	480(s), 420(s)	270(s), 220(sh)	28500	16650	10300	1003	1004	0.97	3.21
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Ni}(\text{NCS})_2(\text{nia})_2$	2180(sh), 2100(s)	760(s), 730(sh)	480(m), 420(s)	265(s), 215(m)	26900	16450	10200	1010	866	0.84	3.17
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Co}(\text{NCS})_2(\text{bpy})$	2160(s), 2090(s)	760(s), 730(m)	470(w), 430(s)	235(s), 210(w)	20850	16400	—	855	910	0.93	5.10
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Co}(\text{NCS})_2(\text{nia})_2$	2180(s), 2090(sh)	760(s), 730(w)	480(s), 420(m)	215(s), 205(w)	21105	17110	—	862	857	0.88	5.24
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Cu}(\text{NCS})_2(\text{bpy})$	2150(s), 2080(sh)	750(s), 720(sh)	470(w), 410(s)	260(m), 210(w)	—	—	—	—	—	—	2.03
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Cu}(\text{NCS})_2(\text{nia})_2$	2140(s), 2080(s)	750(m), 720(s)	470(w), 420(s)	265(s), 240(w)	—	—	—	—	—	—	2.16
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Zn}(\text{NCS})_2(\text{bpy})$	2130(s), 2090(s)	780(s), 735(m)	460(m), 410(s)	225(s), 210(sh)	—	—	—	—	—	—	—
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Zn}(\text{NCS})_2(\text{nia})_2$	2140(s), 2080(s)	760(m), 740(s)	465(s), 430(m)	220(s)	—	—	—	—	—	—	—
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Mn}(\text{NCS})_2(\text{bpy})$	2120(s), 2010(m)	780(s), 735(s)	470(s), 440(m)	210(s)	—	—	—	—	—	—	6.23
$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Mn}(\text{NCS})_2(\text{nia})_2$	2135(w), 2100(s)	770(w), 720(s)	460(m), 400(s)	215(s)	—	—	—	—	—	—	6.60

s=strong, sh=shoulder, m=medium, w=weak.

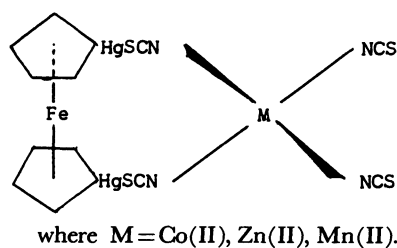


Fig. 1.

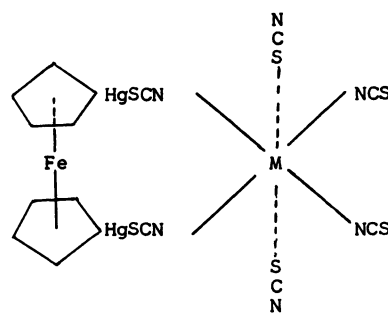


Fig. 2.

presence of octahedral coordination geometry around nickel. The electronic spectra and the magnetic moment values where M is Cu(II) are also indicative of the presence of octahedral coordination geometry around Cu(II). Both these metal ions acquire octahedral geometry through axial coordination.<sup>9</sup> These complexes are nonconducting in dimethyl sulfoxide. On the basis of these results the structure as shown in Fig. 2 can be proposed.

**Adducts:**  $\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{M}(\text{NCS})_2\text{L}_x$  ( $x=2$  when L is nia and 1 when bpy). The coordination number of M in the Lewis acid where M is Co(II), Zn(II), or Mn(II) is four against the maximum of six. Due to this unsaturation at M, they have been named as Lewis acid. Where M is Ni(II) or Cu(II) the coordination number

six has been achieved through weak axial bonding which can easily be replaced by ligands. Accordingly both types of Lewis acids have been reacted with nicotinamide and 2,2-bipyridyl and adducts of general formula  $\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{M}(\text{NCS})_2\text{L}_x$  have been prepared.

The infrared spectra of the adducts where M is Ni(II) or Cu(II) show that there is no significant change in the positions of  $\nu(\text{CN})$ ,  $\nu(\text{CS})$ ,  $\delta(\text{NCS})$ , and  $\nu(\text{M-NCS})$  bands. This shows that the bridging nature of thiocyanate and octahedral coordination geometry around M are retained. The infrared spectra of the adducts where M is Co(II), Zn(II) or Mn(II) also show that the

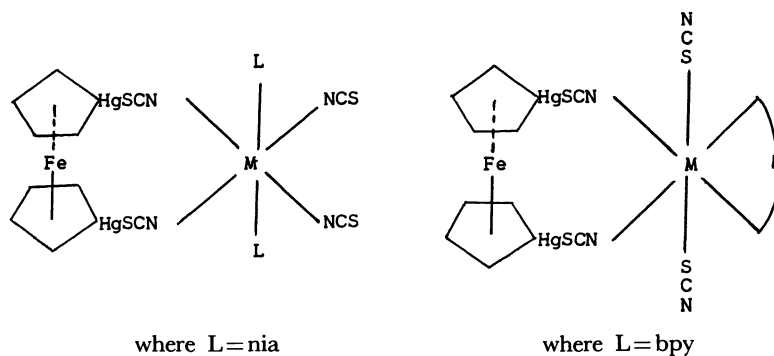


Fig. 3.

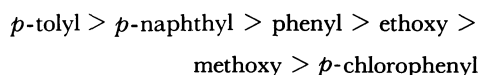
Table 3.  $\Delta E_{nm}^{\dagger}$  Derived from  $E_{n(\text{eff})}^{\dagger}$  of M in  $M(\text{NCS})_2$  and  $E_{m(\text{eff})}^{\dagger}$  of FBMT in the Formation of Lewis Acids

S.No.	Lewis Acid	$E_{n(\text{eff})}^{\dagger}$ of M in $M(\text{NCS})_2$	$E_{m(\text{eff})}^{\dagger}$ of FBMT	$\Delta E_{nm}^{\dagger}$	CFSE	Matching Constant $\Delta E_{nm}^{\dagger} + \text{CFSE}$
1.	$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Ni}(\text{NCS})_2$	-3.10	-11.16	8.06	6.66	15.72
2.	$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Co}(\text{NCS})_2$	-3.56	-11.16	7.60	4.55	12.15
3.	$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Zn}(\text{NCS})_2$	-4.92	-11.16	6.24	—	6.24
4.	$\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{Mn}(\text{NCS})_2$	-9.01	-11.16	2.15	—	2.15

bridging nature of the thiocyanate is retained but a negative shift is observed in  $\nu(\text{M}-\text{NCS})$  band. This negative shift is on account of change in tetrahedral geometry around M to octahedral.<sup>8,10</sup> Such a change is not observed where M is Ni(II) or Cu(II), because the geometry around M, in these cases, remains octahedral in the Lewis acid and the adducts as well. The electronic spectral data of all adducts, their assignments, various spectral parameters, and magnetic moment values, as presented in Table 2, indicate that the coordination geometry around M is octahedral. All the adducts are nonconducting in nature. On the basis of these results the structure as shown in Fig. 3 can be proposed for the adducts.

#### Comparison with the Complexes of $\text{RHgSCN}$ :

(R = *p*-tolyl, *p*-naphthyl, phenyl, ethoxy, methoxy, *p*-chlorophenyl).  $\text{RHgSCN}$  have been reported to act as Lewis bases towards  $\text{M}(\text{NCS})_2$ . The base strength of  $\text{RHgSCN}$  changes on change of R. The following sequence of base strength on the basis of various physicochemical studies has been established.<sup>11</sup>



The FBMT also acts as a base towards  $\text{M}(\text{NCS})_2$ . This base has two thiocyanato groups as donor sites, and consequently the complexes formed by this base are more stable. The  $D_q$  values of Co(II) and Ni(II) Lewis acids are  $541\text{ cm}^{-1}$  and  $1020\text{ cm}^{-1}$ . These values are higher than the  $D_q$  values of the corresponding complexes of the  $\text{RHgSCN}$ . This fact is also demonstrated experimentally. The thiocyanato bridge between Hg(II) and M(II) in the Lewis acids of  $\text{RHgSCN}$  is ruptured on reaction with 2,2'-bipyridyl, resulting in the for-

mation of cationic-anionic complexes of general formula  $[\text{M}(\text{bpy})_3][\text{RHg}(\text{SCN})_2]_2$ . The Lewis acids of the present series, however, form adducts on such a reaction, and the thiocyanato bridge between M(II) and Hg(II) is retained. This shows that the base strength of this compound is higher than any of the  $\text{RHgSCN}$ .

**Quantitative Softness Parameters:** The effective softness  $E_{n(\text{eff})}^{\dagger}$  value of M in  $\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{M}(\text{NCS})_2$ ,  $E_{m(\text{eff})}^{\dagger}$  value of N-end of nicotinamide and 2,2'-bipyridyl and of N-end of FBMT have been evaluated by the method described elsewhere,<sup>12</sup> and the results are included in Table 3. The FBMT reacts with  $\text{M}(\text{NCS})_2$  and forms Lewis acid of general formula  $\text{Fe}(\text{C}_5\text{H}_4\text{HgSCN})_2\text{M}(\text{NCS})_2$ . The difference ( $\Delta E_{nm}^{\dagger}$ ) between  $E_{m(\text{eff})}^{\dagger}$  of N-end of FBMT and  $E_{n(\text{eff})}^{\dagger}$  of M in  $\text{M}(\text{NCS})_2$  have been evaluated by the following equation:

$$\Delta E_{nm}^{\dagger} = \left| E_{n(\text{eff})}^{\dagger} - E_{m(\text{eff})}^{\dagger} \right|$$

The  $\Delta E_{nm}^{\dagger}$  value is the highest when M is Ni(II) and the lowest when Mn(II). The  $\Delta E_{nm}^{\dagger}$  between  $E_{n(\text{eff})}^{\dagger}$  of M in Lewis acids and  $E_{m(\text{eff})}^{\dagger}$  of nicotinamide and 2,2'-bipyridyl and the matching constant values have been derived in order to find out which out of the two ligands forms more stable bond with M and which out of the various M forms more stable bond with nicotinamide or bipyridyl. The results are included in Table 3. The  $\Delta E_{nm}^{\dagger}$  values show that bipyridyl forms more stable M-L bond than nicotinamide which is in concurrence with the established fact.  $\Delta E_{nm}^{\dagger}$  values are the highest when M = Ni(II) and the lowest when M = Mn(II). The sequence with other M is as follows:

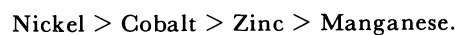


Table 4.  $\Delta E_{nm}^{\dagger}$  Derived from  $E_{n(eff)}^{\dagger}$  of M in  $Fe(C_5H_4HgSCN)_2M(NCS)_2$  and  $E_{m(eff)}^{\dagger}$  of the Ligand in the Formation of Adducts

Complex	$E_{n(eff)}^{\dagger}$ of M in Lewis Acid	$E_{m(eff)}^{\dagger}$ of nia	$\Delta E_{nm}^{\dagger}$	CFSE	Matching Constant	log K
$Fe(C_5H_4HgSCN)_2Ni(NCS)_2(nia)_2$	-2.28	-11.47	11.49	6.42	17.91	5.16
$Fe(C_5H_4HgSCN)_2Co(NCS)_2(nia)_2$	-2.83	-11.47	10.94	4.29	15.23	5.09
$Fe(C_5H_4HgSCN)_2Zn(NCS)_2(nia)_2$	-4.11	-11.47	9.66	—	9.66	4.92
$Fe(C_5H_4HgSCN)_2Mn(NCS)_2(nia)_2$	-8.90	-11.47	4.87	—	4.87	4.43

nia = nicotinamide.

The stability of metal ligand bond in case of transition metal ions has been expressed in terms of matching constant, by adopting the following relation:

$$\text{Matching constant} = \Delta E_{nm}^{\dagger} + \text{CFSE}$$

The matching constant values are presented in Table 4, along with thermodynamic stability constant (log K). Both the values indicate that most stable M-L bond is formed where M is Ni(II) and sequence is as follows:

Nickel(II), Cobalt(II), Zinc(II), and Manganese(II).

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